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Inorganic Polymers of the Main-Group Elements

by

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Inorganic Polymers of the Main-Group Elements

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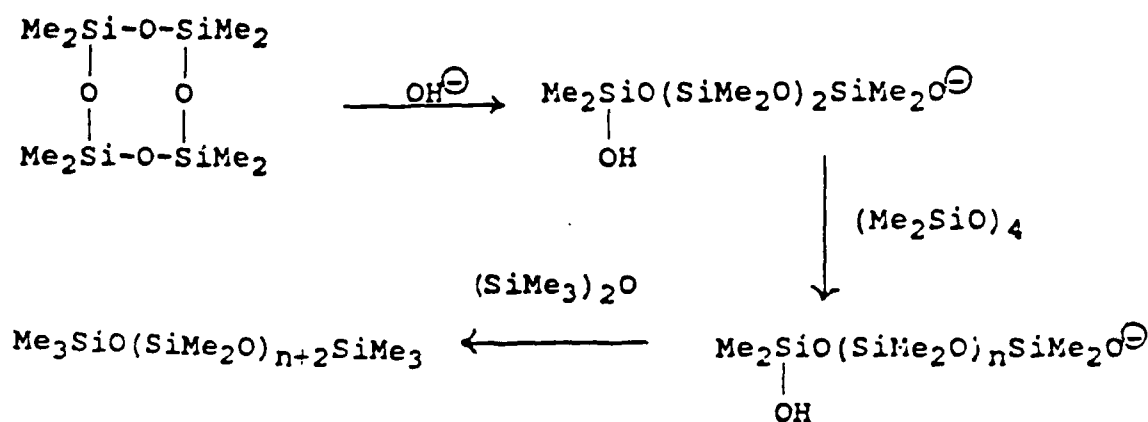
Presented at the NEACT Summer Conference, University of Massachusetts, Amherst Massachusetts, August 1987.

While to most chemists polymers belong to the domain of organic chemistry, there are interesting and useful polymers which are best considered as inorganic or hybrid inorganic-organic systems. The purpose of this article is to acquaint you with some of these materials which are attracting commercial and academic interest. The focus will be primarily on synthetic linear polymers involving main-group elements, specifically poly(siloxanes), $(R_2SiO)_n$, poly(phosphazenes), $(R_2PN)_n$, poly(organosilanes), $(R_2Si)_n$, and poly(sulfur-nitride), $(SN)_n$. It is important to recognize that even this selection represents a small subset of a larger group of synthetic and naturally occurring materials which include linear oxyanions (e.g. silicates, phosphates and borates), two dimensional solids (e.g. sheet silicates) and network solids (e.g. silicon carbide, silicon nitride, boron nitride).

Synthesis

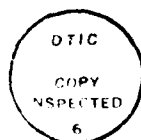
The best known and most commercially important system under discussion is the poly(siloxanes) which are more familiarly known as silicones. The synthesis of these materials starts with the Rochow process in which methyl chloride is passed over silicon

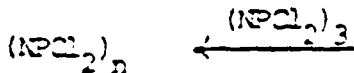
which is dopped with copper. The resulting dichlorodimethylsilane, Me_2SiCl_2 , is hydrolyzed to yield $(\text{Me}_2\text{SiO})_4$. The cyclic siloxane undergoes ring opening polymerization with acid or base catalysis to give the poly(siloxanes). The pattern of formation of a cyclic material



followed by ring-opening polymerization is repeated in the classic poly(phosphazene) synthesis. The ammolysis of PCl_5 leads to a range of cyclophosphazenes, with the six-membered ring predominating. Thermal polymerization of this material is believed to proceed through initial heterolytic phosphorus-chlorine bond cleavage. The resulting phosphonium ion initiates ring opening polymerization.

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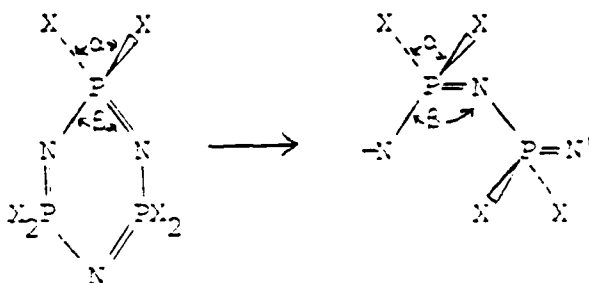



$$\text{SCl}_2 \xrightarrow{\text{NH}_3} \text{S}_4\text{N}_4 \xrightarrow[\Delta]{\text{Ag}} \begin{array}{c} \text{N}-\text{S} \\ | \quad | \\ \text{S}-\text{N} \end{array} \longrightarrow (\text{SN})_n$$
$$\begin{array}{ccc} \text{H} & & \text{H} \\ | & & | \\ \text{H}_2\text{C}=\text{CH}-\text{Cl} & \xrightarrow{\text{Na}} & \text{H}-\text{C}-\text{C}-\text{H} \\ | & & | \\ \text{H} & & \text{H} \end{array}$$

In all of the synthetic chemistry described above there is a balance between ring and linear chain formation. At each step, the growing chain can either add another monomer unit or undergo cyclization. The tendency towards cyclization will be particularly noteworthy when the growing chain has functionality at each end. Some of the factors involved in these processes can be understood in terms of simple thermodynamic arguments. Both entropy and enthalpy terms can be significant so we will consider each in turn. Cyclization will be an entropy favored process. A specific example to illustrate this point is shown below wherein a linear siloxane cyclizes by elimination of water thereby



increasing the number of molecules in the system (and hence the total disorder). The enthalpy term is more complex in that both skeletal and side group effects are important. The major skeletal effect is ring strain. The stable cyclic species formed is usually the one with minimum ring strain. In the case of linear siloxanes, the silicon-oxygen-silicon bond angle is larger than the corresponding carbon analog, so larger rings, e.g. $(\text{Me}_2\text{SiO})_4$, are favored. Ring strain is relieved by ring opening to the linear species. The contributions of the side groups to



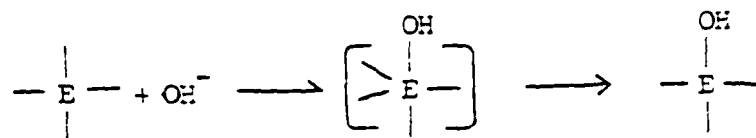
the enthalpy term are also important. If one considers the changes in the endo-(β) and exocyclic (α) bond angles in the ring opening polymerization, we see a decrease in α with an increase in β . This observation correlates nicely with the fact that large exocyclic groups which force a large α value inhibit polymerization and favor depolymerization to cyclic species.

High and Low Temperature Behavior

Stability under extreme conditions has traditionally been an important property of inorganic polymer systems. As far back as 1941 Rochow stated (in a patent application): "high heat stability would call for a polymer having a minimum of organic content". Stability, however, is an ubiquitous term and one must be more precise as to what factors are of importance. In a thermodynamic approach, there are two major points to consider. The bond enthalpy of the backbone chain atoms can be a significant consideration, e.g. the carbon-carbon and silicon-oxygen bond enthalpies are 347 and 444 kJ/mole respectively thus bond enthalpy makes a major contribution to the thermal stability of the poly(siloxanes). The poly(phosphazenes), several of which rival the poly(siloxanes) in high temperature stability, have a backbone bond enthalpy of 318 kJ/mole so clearly other important contributions to polymer stability must be explored. The other major thermodynamic consideration is what degradation pathways are energetically available for a given class of polymers. The oxidation of a carbon-carbon bond to ketones, for example, is very exothermic (approximately 381 kJ/mole), thus leading to

oxidative instability. These particular pathways are not available for poly(siloxanes) and poly(phosphazenes) in which the heteroatoms are already in their highest oxidation state, hence they exhibit improved oxidative stability.

Another important factor is kinetic stability. Ironically, many of the common backbone units used in non-metal inorganic polymers are susceptible to hydrolysis reactions. Since pentacoordinated derivatives of second row elements (e.g. Si,P) are well known, stable materials, the low activation energies which are noted for formation of pentacoordinated intermediates in hydrolysis reactions are understandable. This fundamental



E = Si, P

problem is overcome by building up sufficient steric crowding about the backbone from the organic groups on the side chain to render the second row atom inaccessible to the degradative reagents. As an example of the effectiveness of this approach, poly(phosphazenes) with alkoxy or aryloxy side chains, $[NP(OR)_2]_n$, can be stored for long periods of time in concentrated acid or base without noticeable degradation. This is in contrast to the parent polymer, $(NPCl_2)_n$, which undergoes facile hydrolysis from atmospheric moisture.

Turning our attention to the other thermal extreme, main-group inorganic polymers often exhibit superior flexibility at low temperatures. The fundamental parameter used to measure this

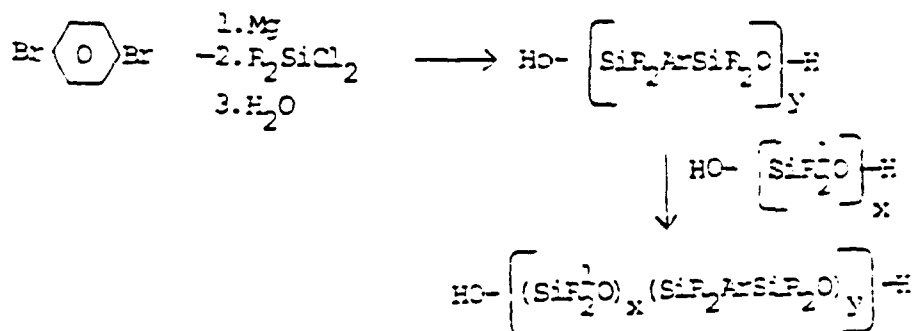
effect is the glass transition temperature, T_g , which is simply the temperature at which a material passes from a brittle (glass) state to a flexible (plastic) form. At the molecular level, the flexibility of polymer chains is due to torsional mobility, i.e., rotation about the backbone bonds. The torsional mobility, in turn, depends on the inherent rotational barrier about the backbone bond and the interaction between side groups. The rotational barriers about the silicon-oxygen and phosphorus-nitrogen bonds are exceptionally low and therefore poly(siloxanes) and poly(phosphazenes) often retain flexibility at low temperatures. This property when combined with the aforementioned high temperature stability makes these polymers the high-tech materials of choice for items such as o-rings, gaskets, fuel-lines etc., which must operate at either temperature extreme or over a broad temperature range. The effect of side groups on T_g is dramatically demonstrated in the poly(phosphazene) series shown below:

Polymer	$(Cl_2PN)_n$	$[(-O)_2PN]_n$	$[(PhO)_2PN]_n$	$[Me_2N)_2PN]_n$	$[(PhNH)_2PN]_n$
$T_g(^{\circ}C)$	-66	-64	6	-4	105

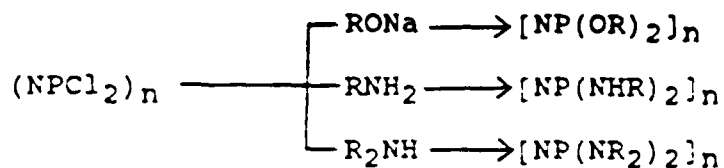
One can see the effect of increasing the steric crowding (hence hinderance of rotation) on T_g by comparing the ethoxy and phenoxy derivatives. The dramatic effect of side-chain hydrogen bonding is seen in the anilino derivative.

Reactivity and Property Design

Reactions of polymers are often carried out in order to effect specific property changes. Even though the reactions under consideration are actually polymerization processes, the first case of property design will focus on changes in backbone structure. The thermal degradation of poly(siloxanes) often involves reversion to cyclosiloxanes. If one could incorporate a rigid function, such as a phenyl group, into the backbone, the tendency to form cyclic materials would be suppressed. The reaction sequence leading to these poly(silarylene siloxane)s, which indeed do show increased thermal stability, is shown below.



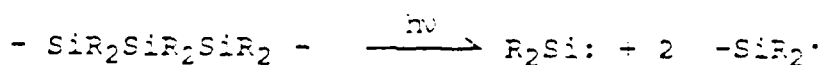
Going on to actual reactions of polymers, the chemistry of the poly(phosphazenes) presents a classic case of side group modification by reactions of a polymeric precursor. Due to its hydrolytic instability poly(dichlorophosphazene), $(\text{NPCl}_2)_n$, was little more than a laboratory curiosity. However, nucleophilic substitution reactions leading to replacement of the chlorine atoms with alkoxy, aryloxy and amino functions lead to polymers, some of which are commercial products, with high stability and a broad range of T_g values (see above).



$$n \sim 15,000$$

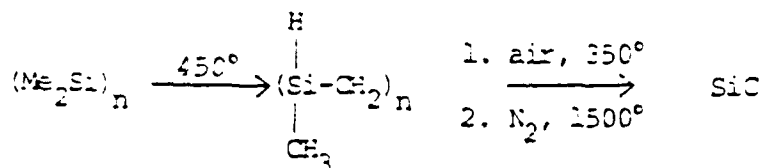
The reactions of poly(phosphazenes) are not limited to displacement at phosphorus. Numerous examples now exist of two step processes in which a complex organic functionality is first attached by reactions of the type shown above. Further reactions are carried out on the side group moiety in order to introduce catalytically or biomedically active units thus using the poly(phosphazene) as a support for these particular processes.

While the reactions described above involve a certain amount of synthetic strategy and subtlety, the remain types of reactions are degradative in nature, often under forcing conditions. The first example of this type of process is the photodegradation of poly(organosilanes). The combination of the weak silicon-silicon bond and its ability to act as a chromophore (see below) leads to a rich photochemistry of these polymers. The details of the photodegradation are not fully understood, however both silyl radicals and silylenes (silicon analogs of carbenes) are observed.



The facile photodegradation of poly(organosilanes) has lead to lithographic applications of these polymers for selective

protection of surfaces exposed to oxygen plasma etching. In even more dramatic degradative chemistry, poly(organosilanes) upon thermolysis rearrange to poly(carbosilanes) which upon further pyrolysis are converted to silicon carbide. The use of the polymeric precursor allows for shapes or fibers of the ceramic



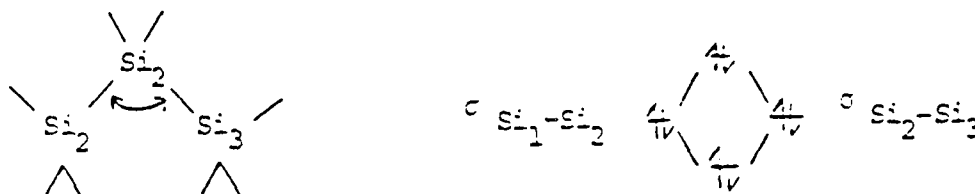
(SiC) to be premolded (or spun) from the linear polymer. Similar pyrolytic routes have been developed for the conversion of poly(silazanes) to silicon-nitride and considerable interest exists in expanding this approach to other ceramic materials.

Electronic Structure

Although there are many interesting and significant problems concerning the electronic structure of main-group inorganic polymers, the focus of this section will be on delocalized electron systems. Poly(sulfurnitride), $(\text{SN})_x$, is a bronze, metallic conductor which becomes superconducting at 0.3°K . The metallic nature of this non-metal polymer is understandable if one starts by considering the electronic structure of the monomer, SN. This species has fifteen valence electrons so, like the isoelectronic NO molecule, it has an unpaired electron. When these units form a polymeric chain, the orbitals containing the unpaired electron combine to form a partially filled conduction band (i.e., a m.o. delocalized along the entire chain) in a manner analogous to that of a metal (e.g. Na) with an unpaired

electron, thereby giving raise to metallic properties.

The poly(organosilanes) present an even more interesting case in that they show strong electronic absorbtion bands in the UV region (300-400 nm). The UV maxima shift to lower energy with increasing chain length thus exhibiting behavior which is typical of a delocalized system. This delocalization of σ electrons is believed to occur via a hyperconjugative mechanism in which adjacent σ silicon-silicon orbitals overlap. The resulting



molecular orbital energy level diagram for a simplified three silicon atom fragment shows how the ground state energy is raised. Similar excited state effects are operative. Awareness of these sorts of interactions allow for a qualitative understanding of both the electronic spectroscopy and photolability of these systems.

The purpose of this short survey has been to introduce some of the more important issues involving synthesis, structure, bonding, energetics and applications of this growing area of chemistry. The interested reader may wish to consult some of the monographs and reviews listed in the bibliography for further elaboration and exposure to topics in inorganic polymer chemistry.

Acknowledgment

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